

Ab initio MOLECULAR DYNAMICS STUDY OF D₂ DESORPTION FROM Si (100)

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Ab initio molecular dynamics calculations of deuterium desorbing from Si(100) have been performed in order to monitor the energy redistribution among the hydrogen and silicon degrees of freedom during the desorption process. The calculations show that part of the potential energy at the transition state to desorption is transferred to the silicon lattice. The deuterium molecules leave the surface vibrationally hot and rotationally cold, in agreement with experiments; the mean kinetic energy, however, is larger than found in experiments.

1 Introduction

Hydrogen adsorption on and desorption from Si surfaces are of great technological relevance for, e.g., the etching and passivation of Si surfaces or the growth of Si crystals (see, e.g., Ref. [1] and references therein). Besides, the dynamics of the hydrogen interaction with Si surfaces is also of fundamental interest due, among others, to the so-called barrier puzzle: While the sticking coefficient of molecular hydrogen on Si surfaces is very small^{2,3,4} indicating a high barrier to adsorption, in desorption experiments an almost thermal energy distribution of the molecules was found⁵ indicating a low barrier to adsorption. In order to explain this puzzle it was suggested to take the strong surface rearrangement of Si upon hydrogen adsorption into account:^{3,6} The hydrogen molecules impinging on the Si substrate from the gas phase encounter a Si configuration which is unfavorable for dissociation, while desorbing hydrogen molecules leave the surface from a rearranged Si configuration with a low barrier in the hydrogen coordinates. The lattice rearrangement energy was assumed to be about 0.7 eV,⁶ a value in reasonable agreement with the transition state energy obtained by cluster calculations.^{7,8,9} Density-functional calculations of the potential energy surface (PES) of H₂/Si (100) using the supercell approach^{10,11} provided a detailed microscopic description of the interaction. The transition state energy was determined to be only $\sim 0.3 - 0.4$ eV with the substrate rearrangement energy being merely $\lesssim 50\%$ of this value.

The calculation of PESs is an important prerequisite for understanding reaction dynamics. For a quantitative analysis, however, a calculation of the dynamics is indispensable. We have therefore performed *ab initio* molecular dynamics calculations to monitor the energy distribution of D₂ molecules desorbing from Si (100). We will show that part of the potential energy at the

barrier position is indeed transferred to the silicon lattice, the mean kinetic energy of desorbing molecules, however, is larger than found in experiments.

2 Computational details

In our *ab initio* molecular dynamics calculations¹² the forces necessary to integrate the classical equations of motion are determined by density-functional calculations. The exchange-correlation functional is treated in the generalized gradient approximation (GGA)¹³. In previous slab studies the total energies were calculated within the local density approximation (LDA) with *a posteriori* GGA corrections¹¹. The main effects of using the GGA in the complete self-consistent cycle are a small increase of the theoretical lattice constant of Si¹⁴ and a slight rise in the barrier height from $E_b = 0.3$ eV¹¹ to $E_b = 0.4$ eV. To correctly represent the up and down buckling of the clean Si(100) surface we use a (2×2) surface unit cell. The Si slab consists of five atomic layers. The topmost three of them are free to move in the molecular dynamics simulations, while the remaining two layers are fixed at their bulk positions. The density-functional calculations are performed with two \mathbf{k} -points in the irreducible part of the Brillouin zone and 40 Ry cutoff energy. The equations of motion are numerically integrated within a predictor-corrector scheme with a time step of 1.2 fs. The calculations have been performed on typically 64 nodes of the Cray T3D of the Konrad-Zuse-Zentrum, Berlin.

3 Results

Since the barrier to associative desorption of hydrogen from Si(100) is rather high ($E_d = 2.5$ eV),¹¹ there is no sense in performing molecular dynamics calculations starting with the deuterium atoms at the adsorption sites because of the extremely low number of desorption events. Therefore we started the desorption trajectories close to the transition state for dissociative adsorption which was determined in the earlier study.¹¹ In total we have computed 40 trajectories of D₂ desorbing from Si(100). Eight trajectories were determined with the Si lattice initially at rest, i.e. at a surface temperature of $T_s = 0$ K, in order to specifically monitor desorption trajectories starting at the transition state. Figure 1 illustrates the strong surface rearrangement of Si(100) upon hydrogen adsorption/desorption. Snapshots of a calculated trajectory are shown in Fig. 1b). The dark Si atoms correspond to the relaxation of the Si lattice after the desorption event. Approximately 0.1 eV of the potential energy at the transition state is transferred to vibrations of the Si lattice which is a rather large amount compared to hydrogen/metal systems.

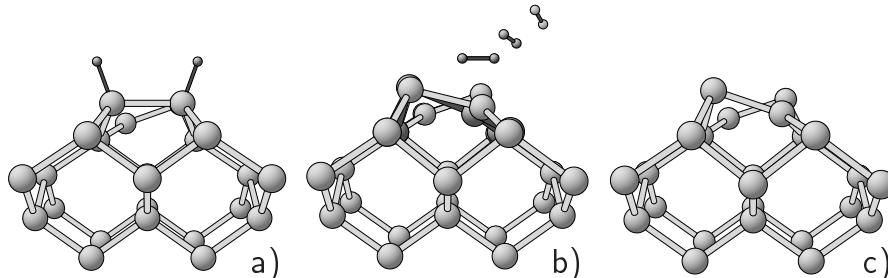


Figure 1: a) Hydrogen covered Si(100) surface (monohydride). b) Snapshots of a trajectory of D_2 desorbing from Si(100) starting at the transition state with the Si atoms initial at rest. The dark Si atoms correspond to the Si positions after the desorption event. c) Clean anti-buckled Si(100) surface.

The desorption experiments determining the mean kinetic energy of D_2 desorbing from Si(100) were done with a rather high surface temperature of $T_s \approx 920$ K. In order to simulate these experimental conditions, we have performed *ab initio* molecular dynamics calculations with initial conditions corresponding to the experimental surface temperature. The system was allowed to equilibrate for more than 500 fs, whereby the deuterium atoms were kept close to the transition state by an additional cage-like potential. The additional potential was then switched off and the energy distribution of the D_2 molecules desorbing from the thermal surface were monitored. In total 32 “thermal” desorption trajectories were calculated. The mean total, kinetic, vibrational, and rotational energies of the desorbing molecules are listed in Table 1 (note that $k_B T_s = 0.079$ eV).

The results show vibrational heating, i.e. $\langle E_{vib} \rangle > k_B T_s$, and rotational cooling, i.e. $\langle E_{rot} \rangle < k_B T_s$, in agreement with the experiment.¹⁵ The mean kinetic energy, however, is much larger than the experimental value of $\langle E_{kin} \rangle^{exp} = 0.165$ eV. The difference between the experimental and theoretical results corresponds roughly to the barrier height E_b . A closer analysis of the trajectories¹⁶ reveals that still approximately 0.1 eV of the potential energy at the transition state is transferred to the Si lattice, however, due to the Si lattice vibrations the mean adsorption barrier is increased by roughly the same amount. Possible contributions to the discrepancy between theory and experiment could be: (i) insufficient statistics, i.e., too few trajectories computed, (ii) quantum mechanical effects (e.g., tunneling and zero-point effects) not taken into account in the classical molecular dynamics, (iii) dissipation chan-

Table 1: Mean energy distribution averaged over 32 trajectories of D₂ molecules desorbing from a Si(100) surface at a surface temperature of $T_s = 920$ K.

$\langle E_{tot} \rangle$	0.72 ± 0.17 eV	$\langle E_{vib} \rangle$	0.11 ± 0.09 eV
$\langle E_{kin} \rangle$	0.58 ± 0.13 eV	$\langle E_{rot} \rangle$	0.03 ± 0.05 eV

nels not considered, e.g., electronic excitations, (iv) limitations of the GGA functional, (v) experimental uncertainties. Certainly there is a strong need for future theoretical and experimental studies of the hydrogen on silicon system.

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